

CHLORINE CATALYZED DESTRUCTION OF OZONE: IMPLICATIONS FOR OZONE VARIABILITY IN THE UPPER STRATOSPHERE

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Abstract. The annual mean and the annual amplitude of ozone have been derived from ozone measurements from the SBUV and SBUV/2 spectrometers on board the Nimbus-7 and NOAA-11 satellites. These values differ significantly from values calculated using a two-dimensional model of stratospheric photochemistry and dynamics with standard chemistry. We have found that the differences between the calculated and data-derived values are considerably improved by changing the partitioning in the Cl_y family to create a larger reservoir of HCl and reducing ClO. This is accomplished by including a channel for the products $\text{HCl} + \text{O}_2$ from the reaction $\text{ClO} + \text{OH}$ in addition to the products $\text{Cl} + \text{HO}_2$. This partitioning also improves the agreement between the calculated and measured values of ClO/HCl ratio.

Introduction

A longstanding model/measurement discrepancy has been the underestimate of ozone abundance in the upper stratosphere by model simulations compared to observations (e.g., Johnston and Podolske, 1978; Jackman et al., 1986). Although the use of updated reaction rates and more realistic levels of Cl_y (Cl , ClO , HCl , HOCl , ClONO_2) in the stratosphere has reduced the model/measurement differences (Natarajan and Callis, 1989; Eluszkiewicz and Allen, 1992), significant systematic disagreements remain.

Suggestions to minimize the differences between the observed and calculated values of ozone include increasing the production rate and decreasing the loss rate of odd oxygen by changing the photolysis and the chemical loss rates of the key reactions within the range of their measured uncertainties (Eluszkiewicz and Allen, 1992). The model ozone response to temperature must also match observations, which provides an additional constraint to the changes which may be made to improve the agreement between the ozone mean values.

Photochemical models also underestimate HCl and overestimate ClO concentration near 40 km as indicated from recent measurements of these constituents from the Atmospheric Trace Molecular Spectroscopy experiment on Spacelab 3 (McElroy and Salawitch, 1989; Natarajan and Callis, 1991; Allen and Delitsky, 1991) and balloon borne microwave spectrometers (Stachnik et al., 1992). McElroy and Salawitch (1989) suggest that a channel for reaction of ClO with OH to form HCl and O_2 in addition to the formation of Cl and HO_2 may be a significant factor in reducing the discrepancy between the measured and calculated values of ClO/HCl.

The purpose of this paper is to assess the significance of changing the ClO/HCl ratio by including the

$\text{ClO} + \text{OH} \rightarrow \text{HCl} + \text{O}_2$ reaction in 2D model simulations in the context of ozone variability in the upper stratosphere. This reaction or any other reaction which increases HCl at the expense of ClO also has the potential of reducing the discrepancy between the measured and observed values of ozone near 40 km as it tends to reduce the chlorine catalyzed loss rate of odd oxygen. The long term trends, the seasonal cycle, and the annual mean calculated for ozone all depend on the importance of chlorine catalyzed ozone loss in the ozone balance.

Data Description

The data used for this study consist of monthly values of ozone mixing ratio at 2 mb (~45 km) derived from the Nimbus-7 SBUV and NOAA-11 SBUV/2 spectrometers. They are zonally averaged in 10° intervals from 80°S to 80°N . The SBUV/2 spectrometer on NOAA-11 is an improved version of the Nimbus-7 SBUV instrument (Fleig et al., 1990). Both the instruments are nadir viewing double monochromators designed to measure total column ozone and ozone mixing ratio over the altitude range 30-0.5 mb (~25-55 km). Nimbus-7 SBUV data has recently been reprocessed to account for the long term instrument drift caused by the degradation of the diffuser plate (Taylor et al., 1992). The reprocessed data cover a 12 year time period (January 1979-December 1990) and overlap with the NOAA-11 data over a two year period from January 1989 to December 1990. Unfortunately, because of the instrument problems, the Nimbus-7 SBUV data after 1986 are relatively more noisy. After February 1987, small chopper synchronization errors had the effect of introducing about 3% of "noise" in the SBUV instruments (R. McPeters, personal communication). The SBUV data also had several missing days during the 1989-90 periods which were linearly interpolated before calculating monthly averages. In comparison, the NOAA-11 SBUV/2 data is

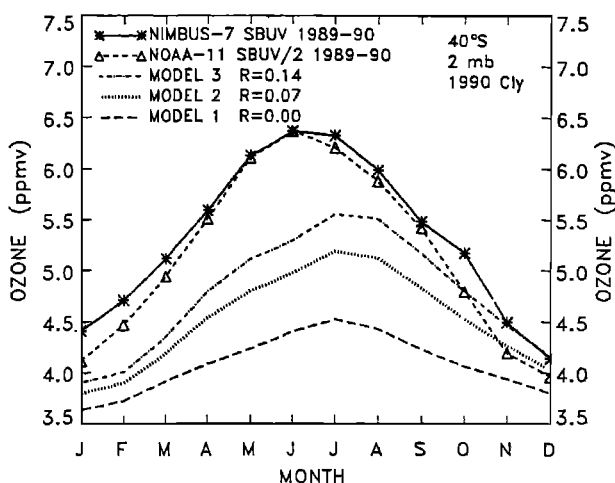


Figure 1. Seasonal variations of ozone at 2 mb and 40°S from observations in 1989-90 (Nimbus-7 SBUV and NOAA-11 SBUV/2) and 2D model simulations with 1990 Cl_y levels (models 1, 2 and 3, described in the text).

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less noisy and almost continuous over the time periods of this study.

Model Description

The two-dimensional (2D) model of stratospheric photochemistry and dynamics used in this study is described by Douglass et al. (1989) and Jackman et al. (1990). Its vertical range, equally spaced in log pressure, is from the ground to approximately 90 km (0.0024 mb) with about a 2 km grid spacing and from 85°S to 85°N with a 10° grid spacing. The temperature field used in the model is derived from 4 years (1979-1982) of National Meteorological Center (NMC) data for the Northern Hemisphere and two years (1979-1980) for the Southern Hemisphere for levels below 0.4 mb, and from the COSPAR International Reference Atmosphere (CIRA, 1972) for levels above 0.4 mb. The methodology for computing the climatological temperature field used in the model is described as follows: values for January, April, July, and October were computed from seasonal three month averages (DJF, MAM, JJA, SON, respectively). The remaining 8 months were then filled in by linear interpolation. Because the advection and horizontal diffusion (K_H) fields are computed directly from the temperature fields, this methodology of using three month seasonal averages effectively eliminates any biases caused by individual monthly averages.

The 2D model was integrated 20 years to reach a repeating annual cycle for several steady-state simulations, described as follows: A base scenario using standard chemistry from DeMore et al. (1990) (referred to as model 1); and two sensitivity studies using standard chemistry, but including the $\text{ClO} + \text{OH}$ reaction for creation of the products $\text{HCl} + \text{O}_2$ using a branching ratio of 0.07 (model 2), and the upper limit branching ratio of 0.14 (model 3) (see DeMore et al., 1990). The model was run for these three scenarios, each using two different Cl_y levels corresponding to years 1980 and 1990. The ground boundary conditions for the source gases were taken from WMO (1990) for 1980 and 1990. Total chlorine in source gases at the ground was 2.5 ppbv in 1980 and 3.5 ppbv in 1990.

Results and Discussion

Figure 1 compares the observed seasonal variations of ozone mixing ratio at 2 mb with the 2D model scenarios

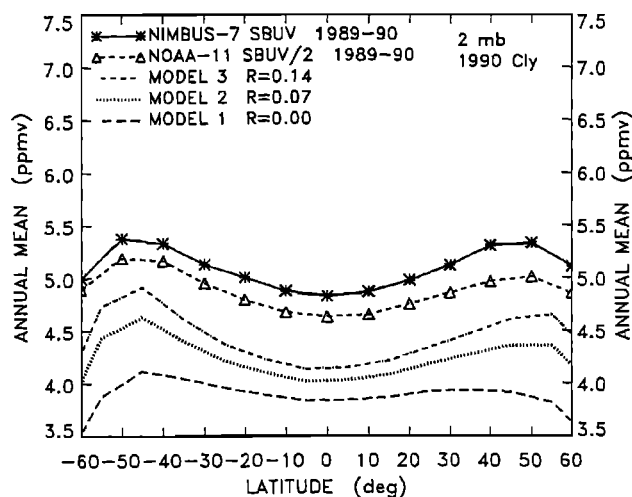


Figure 2. Annual mean of ozone at 2 mb from observations in 1989-90 (Nimbus-7 SBUV and NOAA-11 SBUV/2) and 2D model simulations with 1990 Cl_y levels (models 1, 2 and 3).

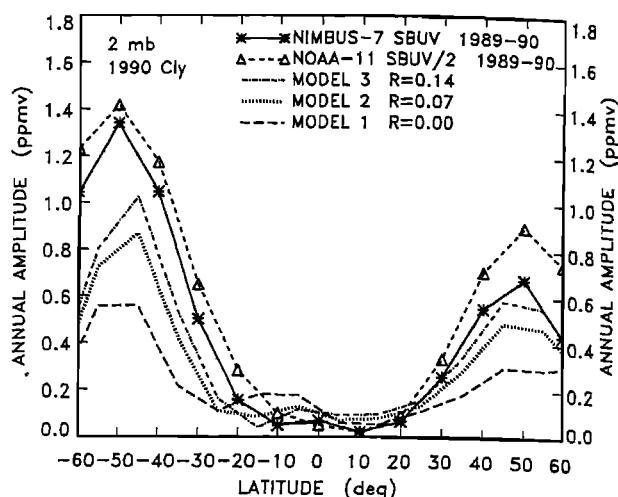


Figure 3. Annual amplitude of ozone at 2 mb from observations in 1989-90 (Nimbus-7 SBUV and NOAA-11 SBUV/2) and 2D model simulations with 1990 Cl_y levels (models 1, 2 and 3).

with 1990 Cl_y levels as described in the preceding section. The comparison is made at 40°S and includes both the NOAA and the Nimbus data averaged over the two year period 1989-90. A two year average is used to minimize the interannual variability associated with the quasi-biennial oscillations and allows a more realistic comparison with the model, which uses a seasonally varying climatological temperature field as input.

The seasonal variations in ozone inferred from the two data sets are similar and show the well known characteristics of ozone mixing ratio at mid-latitudes in the upper stratosphere - a predominant annual cycle with a winter maximum and summer minimum. The annual cycle in ozone is mostly a manifestation of the radiatively driven annual cycle in temperature. The ozone varies inversely as temperature through the temperature dependence of reactions which destroy odd oxygen (e.g., Jackman et al., 1991).

Figure 1 shows that model 1 with standard chemistry and a branching ratio (defined as R) of 0.00 significantly underestimates both the absolute magnitude and the amplitude of the annual cycle. There is considerable improvement with the inclusion of the $\text{ClO} + \text{OH} \rightarrow \text{HCl} + \text{O}_2$ reaction with a branching ratio $R=0.07$ (model

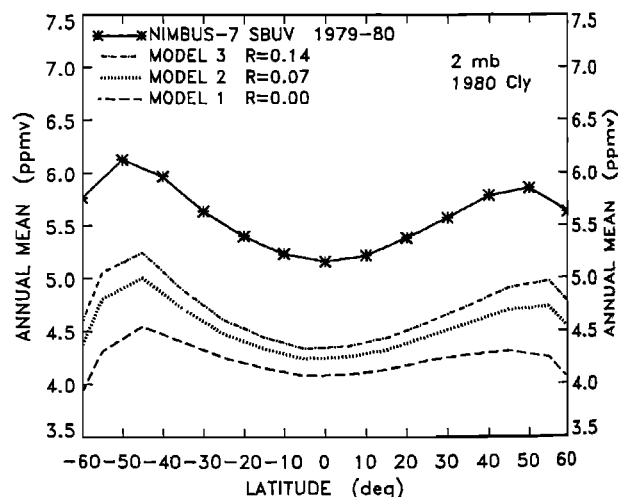


Figure 4. Annual mean of ozone at 2 mb from observations in 1979-80 (Nimbus-7 SBUV) and 2D model simulations with 1980 Cl_y levels (models 1, 2 and 3).

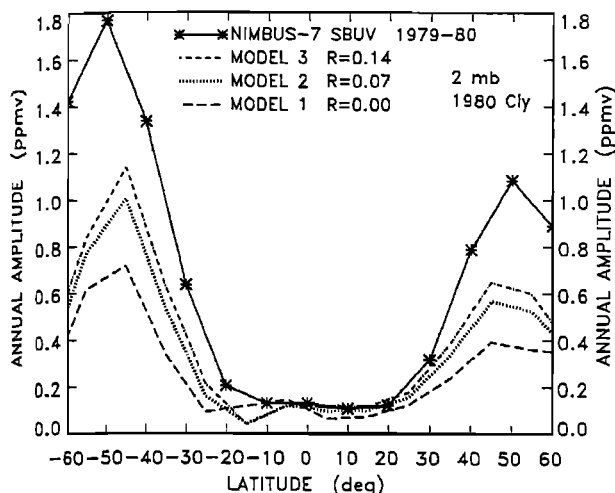


Figure 5. Annual amplitude of ozone at 2 mb from observations in 1979-80 (Nimbus-7 SBUV) and 2D model simulations with 1980 Cl_2 levels (models 1, 2 and 3).

2), and further improvement is seen by using the reaction with the upper limit branching ratio $R=0.14$ (model 3). For example, both the NOAA and Nimbus data show a peak value of about 6.4 ppmv during June (southern winter). Model 1 is about 30% lower than the observed values, whereas model 2 reduces the discrepancy to 21%, and model 3 to about 15%.

The amplitude and phase of the calculated ozone in Figure 1 is determined by the temperature climatology used in the model which exhibits a one month phase shift relative to the individual monthly observations. For example at 2 mb and 40°S, the model temperature maximum and minimum occur in January and July, respectively, compared to December and June for the individual monthly averaged NMC data. This is reflected in the phase difference between the model calculated ozone and the Nimbus-7 and NOAA-11 observations seen in Figure 1. The three-month averaged temperature climatology used in the model differs in magnitude from the individual monthly averaged NMC data by 2-4K, producing an uncertainty of 2-4% in the model calculated ozone field at 2 mb. However, this uncertainty is quite small relative to the large systematic differences between the model-calculated ozone field and observations seen in Figure 1, and does not affect the results of this study.

The differences in magnitude between observations and the three model scenarios are similar to Figure 1 at other latitudes. This is illustrated in Figures 2 and 3 for the annual mean and the annual amplitude that correspond to the zeroth and the first harmonics of the seasonal cycles, respectively. The annual means of ozone mixing ratio at 2 mb inferred from the NOAA data are systematically lower than the Nimbus data by 5-6% at all latitudes between $\pm 60^\circ$ latitude. These differences are well within the uncertainties of the two instruments arising from their initial calibration and the correction for the degradation of the SBUV diffuser plate. When compared with the Space Shuttle backscatter ultraviolet (SSBUV) measurements of ozone (Hilsenrath et al., 1992), both SBUV and SBUV/2 show agreement to 2-3% (Hilsenrath, personal communication). As in Figure 1, model 1 ozone is deficient by about 25-30% at all latitudes with respect to the two data sets. Model 1 also does not accurately reproduce the observed equatorial minima and is relatively constant between $\pm 40^\circ$ latitude. In comparison, models 2 and 3 reproduce the observed latitudinal variations in ozone quite well and there is a significant reduction in the difference between models 2 and 3 ozone and the data.

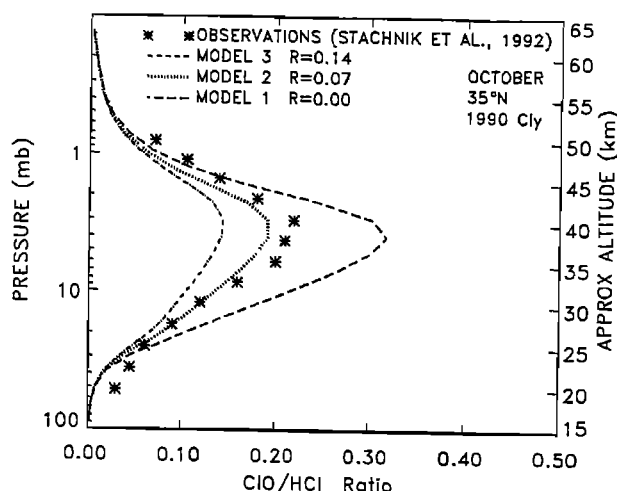


Figure 6. Ratio of ClO/HCl at 35°N for 2D model simulations with 1990 Cl_2 for October compared with observations for October 1991 (Stachnik et al., 1992).

The model 2 and 3 annual amplitude is much closer to the observed annual amplitude at mid and high latitudes in both the hemispheres as seen in Figure 3. For example, at 40°S, the annual amplitude inferred from model 1 is .4 ppmv and is more than a factor of 2 smaller than the observed amplitude of about 1 ppmv. Model 2 yields a value of about .7 ppmv and model 3 gives a value of .8 ppmv, which are both much closer to the observed values. In the tropics, the three models are fairly similar because of the relatively weak annual cycle of temperature. The hemispherical asymmetry both in the data and the models is a manifestation of a similar asymmetry in temperature as discussed extensively in the literature (e.g., Chandra, 1981; Perliski and London, 1989). It should be noted that the agreement between the calculated and observed annual amplitude is more definitive than the agreement of the calculated and observed annual means. The annual amplitude, unlike the annual mean, is not significantly affected by the instrument drift.

The effect of $\text{ClO} + \text{OH} \rightarrow \text{HCl} + \text{O}_2$ reaction for the 1979-80 case is illustrated in Figures 4 and 5. The chlorine in source gases at the ground is assumed to be 2.5 ppbv during this time compared to 3.5 ppbv assumed for 1989-90 case. The two figures compare the annual mean and annual amplitude at 2 mb inferred from the Nimbus-7 SBUV data with the three model scenarios (with $R=0.00, 0.07$, and 0.14). The inclusion of the $\text{ClO} + \text{OH} \rightarrow \text{HCl} + \text{O}_2$ reaction brings the model results in closer agreement with the observations as in Figures 2 and 3. Models 2 and 3 do not entirely eliminate the discrepancy between the calculated and observational results. For example, model 3 systematically underestimates the observed annual mean by about 15% at all latitudes.

The inclusion of the $\text{ClO} + \text{OH} \rightarrow \text{HCl} + \text{O}_2$ reaction in the current model, nevertheless, appears to offer a significant advantage, particularly in simulating the annual cycle of ozone in the upper stratosphere. With the current level of chlorine in the atmosphere, the model with the standard chemistry fails to capture the seasonal variation of ozone in the upper stratosphere as seen in Figures 1 and 3. This results from the decrease in temperature sensitivity of ozone with the increasing level of chlorine in the atmosphere. The $\text{ClO} + \text{OH} \rightarrow \text{HCl} + \text{O}_2$ reaction increases the temperature sensitivity by reducing the impact of the chlorine increase.

The inclusion of the $\text{ClO} + \text{OH} \rightarrow \text{HCl} + \text{O}_2$ reaction in the model also brings the calculated ClO/HCl ratio in

closer agreement with observations. Figure 6 shows the height profiles of ClO/HCl ratio at mid-latitudes for the three model scenarios for the 1989-90 case (total chlorine in source gases at the ground = 3.5 ppbv), compared with October 1991 observations of Stachnik et al. (1992). The peak values of the three model cases all occur at about 40 km, similar to observations, and vary by almost a factor of 3, from 0.35 to 0.40 for model 1 to about 0.15 for model 3. It is seen that the chlorine catalyzed loss rate of odd oxygen is overestimated by model 1 with standard chemistry ($R=0.00$), and that model 2 with $R=0.07$ provides the best overall agreement with observations of the ClO/HCl ratio. A similar conclusion is reached by comparing the model results with April 1991 observations of Stachnik et al. (1992).

Summary and Conclusions

Modifying the partitioning of Cl₂ in our 2D model using the reaction $\text{ClO} + \text{OH} \rightarrow \text{HCl} + \text{O}_2$ reduces some of the differences between the calculated and observed values of ozone in the upper stratosphere. The model using the standard chemistry underestimates both the absolute value of ozone and the annual amplitude as inferred from recent ozone measurements from the SBUV and SBUV/2 spectrometers on board Nimbus-7 and NOAA-11 satellites. The annual cycle in ozone in the upper stratosphere is driven by the radiatively forced annual temperature variation through the temperature dependent loss rate of odd oxygen. The standard chemistry model underestimate of the annual amplitude is a result of a relatively small ozone sensitivity to temperature. The model and observational discrepancy is considerably improved by changing of Cl₂ family partitioning to a larger reservoir of HCl and reduced ClO by the reaction, $\text{ClO} + \text{OH} \rightarrow \text{HCl} + \text{O}_2$, as suggested by McElroy and Salawitch (1989). This reaction reduces the chlorine catalyzed destruction rate of odd oxygen and, in effect, increases the temperature sensitivity to ozone. It also brings the calculated values of ClO/HCl ratio in better agreement with recent measurements.

The $\text{ClO} + \text{HCl} \rightarrow \text{HCl} + \text{O}_2$ reaction does appear to have some impact in predicting the ozone trend over this decade. The inclusion of this reaction produces a model 3 trend in ozone which is about 0.7 times the model 1 value in the upper stratosphere. This difference is not significant enough to favor one model over the other for short term predictions.

There may be other changes, either of the rates of single reactions such as $\text{Cl} + \text{HO}_2 \rightarrow \text{HCl} + \text{O}_2$, or of sets of reactions, which could produce the change in partitioning of chlorine species which seems to be indicated by the ozone data. Thus it is desirable that the reaction $\text{ClO} + \text{OH}$ be re-examined, and the branching between the products $\text{HCl} + \text{O}_2$ and $\text{Cl} + \text{HO}_2$ be established definitively.

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